Direct Observation of Well-dispersed Pt Nanoparticles inside the Pores of Mesoporous Carbon through the Cross Section of Pt/Mesoporous Carbon Particles

Akari Hayashi, Ken'ichi Kimijima, Junichi Miyamoto, and Ichizo Yagi*
Polymer Electrolyte Fuel Cell Cutting-Edge Research Center, National Institute of Advanced Industrial Science and Technology,
2-41-6 Aomi, Koto-ku, Tokyo 135-0064

(Received January 20, 2009; CL-090072; E-mail: i-yagi@aist.go.jp)

Pt nanoparticles were deposited on mesoporous carbon support using two different Pt precursors, and the difference in mass activity toward oxygen reduction between the two was successfully examined through direct observation of Pt nanoparticles inside the mesopores. Existence of 1-nm-sized Pt particles on the wall of mesopores was observed, and catalytic activity was higher if the size of Pt particles inside the pores was smaller. The size and stability of Pt catalysts encapsulated in nanospace is key for catalytic activity.

Mesoporous materials[1] have received attention, since their pores are possibly used as catalytic nanoreactors if catalysts are successfully deposited within the pores. Encapsulation of catalysts in nanospace is also known to have an advantage on minimizing the coalescence or sintering of catalysts.[2] Among mesoporous materials, mesoporous carbon (MC) is especially interesting owing to its high conductivity, and it could be applied to such things as electrode materials. Even so, successful deposition of catalysts into a small pore less than 10 nm is challenging. MC materials synthesized through mesoporous silica template are well studied, but their pores are normally 2–3 nm, and Pt nanoparticles (usually 2 nm or larger) are deposited on the defects in MC or at the entrance of mesopores.[3,4] Their pores are probably too small to use as catalytic reaction space. More recently, direct synthetic methods of MC through self-organization of surfactants and carbon precursors are being developed.[5–7] The pore size is relatively large such as 10 nm in this method, and pores are three dimensionally ordered.

In our group, we are interested in using such nanospace for a cathodic reaction in polymer electrolyte fuel cells and would like to develop a model of triple phase boundary inside the mesopores. In this nanospace, metal–support interaction is increased, and there is an advantage of minimizing sintering of catalyst particles.[2] It will be key to successfully deposit well-dispersed Pt metal catalysts within the pores. So far, we have developed 2-nm-sized Pt nanoparticle deposited MC with 7–8 nm pores (Pt_{ac}/MC) using platinum(II) acetylacetonate precursor and reported its distinctive catalytic behavior toward oxygen reduction.[8] Recently, Pt_{Cl}/MC was newly synthesized by simply changing a Pt precursor to hydrogen hexachloroplatinate(IV). Here, subscript Cl is used to distinguish which Pt precursor is used, and "Cl" is not involved in actual catalyst content. When mass activity toward oxygen reduction was compared, the reactivity of Pt_{Cl}/MC was higher than that of Pt_{ac}/MC. Here, we have developed a successful method to explain the difference in activity, through the observation at the cross section of Pt/MC particles.

MC powder and Pt_{ac}/MC were synthesized following a method in the literature.[8] Pore size and surface area of MC were 7–8 nm and 600 m^2/g, respectively, and Pt nanoparticles were 2 nm, as stated. Regarding Pt_{Cl}/MC, an acetone solution of hydrogen hexachloroplatinate(IV) hexahydrate (31.5 mg $H_2PtCl_6 \cdot 6H_2O$/1 mL acetone) was added to MC powder (35 mg) drop by drop and further stirred at 60 °C until all the solvent was evaporated. Then, it was transferred to an oven and heated under H_2 flow while increasing the temperature from room temperature up to 300 °C over 2 h. The % Pt in Pt_{Cl}/MC was 27.0% based on thermogravimetric analysis.

With newly prepared Pt_{Cl}/MC, the reactivity toward oxygen reduction as a cathode catalyst was studied and compared with that of previously reported Pt_{ac}/MC.[8] Details of electrochemical analyses and mass activity (A/g Pt) plots of Pt_{Cl}/MC and Pt_{ac}/MC against potential (V vs. RHE) are shown in Supporting Information 1.[9] Here, we are interested in the potential region of 0.75–0.95 V vs. RHE, where kinetic reaction predominates, and mass activity of Pt_{Cl}/MC is higher than that of Pt_{ac}/MC, as seen in Supporting Information 1.

To understand the difference in reactivity, Pt_{Cl}/MC was characterized by transmission electron microscopy (TEM), powder X-ray diffraction (XRD), and nitrogen sorption. Dispersion of 1.5-nm Pt particles on MC was seen through TEM observation. Much larger Pt particles, 8 nm and larger, were also observed (Supporting Information 2).[9] The position of Pt, outside or inside the mesopores, cannot be determined from TEM images, but relative pore volume decreased after the addition of Pt (Supporting Information 3),[9] and so at least some of the Pt was deposited inside the mesopores. Estimated average Pt size from Scherrer's equation using Pt(111) peak in obtained XRD patterns (Supporting Information 4)[9] was 22 nm, and this is because the large particles predominate over small ones on XRD patterns. In contrast to Pt_{Cl}/MC, as reported previously,[8] the size of Pt particles in Pt_{ac}/MC is 2 nm, and Pt particles are much more dispersed on MC support. Therefore, with common characterization methods of material, the difference in reactivity cannot be explained.

Since we believe that successful deposition of Pt particles in the mesopores is key, Pt_{Cl}/MC was embedded by resin and sliced to see the cross section without damaging the pore structure. The cross section was then examined by scanning transmission electron microscopy (STEM). Images of the cross section in dark field are shown in Figures 1a and 1b. The cross section of a whole particle is shown in Figure 1a. The edge of the image indicates the surface of a Pt_{Cl}/MC particle, and the middle part of the image shows the inside of a Pt_{Cl}/MC particle. The area pointed by arrow in Figure 1a was observed by higher magnification (Figure 1b). In the higher magnification image, aggregation of large Pt particles (white spots) is observed in the surface region of the Pt_{Cl}/MC particle, but if we look inside the particle, the condition is totally different. A number of 1 nm or smaller Pt

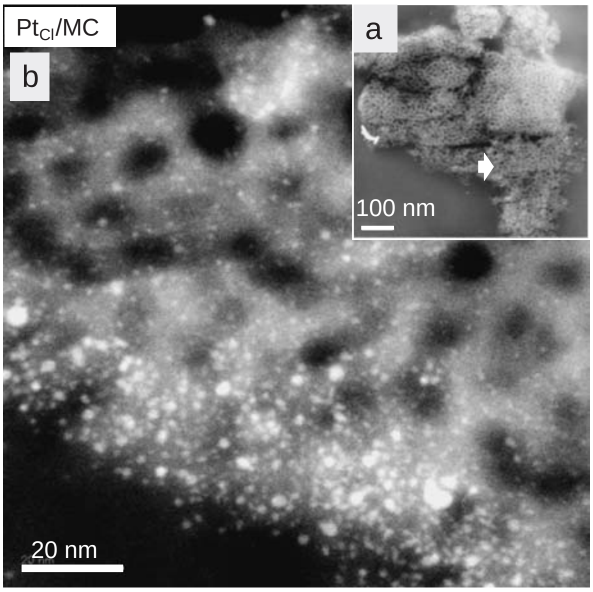

Figure 1. STEM dark field images of Pt_{Cl}/MC cross section. (a) Lower and (b) higher magnifications.

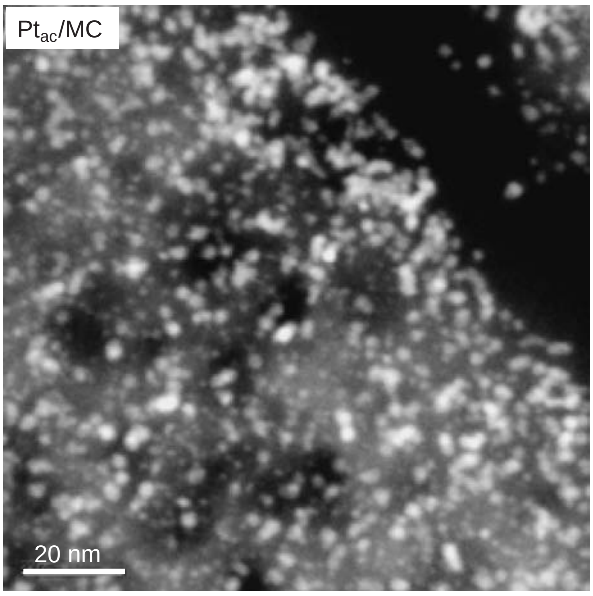

Figure 2. STEM dark field image of Pt_{ac}/MC cross section.

particles were well dispersed (see also Supporting Information 5 and 6).[9] Pt-deposited MC materials were reported by others before,[10–13] but this is the first report actually showing Pt particles inside the pores by looking through the cross section.

Similarly, the cross section of Pt_{ac}/MC was also observed by STEM. As seen in Figure 2, 2-nm-sized Pt particles were well dispersed also inside the mesopores (see also Supporting Information 6).[9] Therefore, Pt_{Cl}/MC with much smaller Pt particles inside the pores has shown higher reactivity than Pt_{ac}/MC with 2-nm-sized Pt particles. We would like to point out that smaller Pt particles are preferred for catalytic reaction owing to their higher surface area, but sintering is always a problem. However, even very small particles (1 nm and smaller) can be stabilized if they are encapsulated inside mesopores, and so small Pt particles can still keep high reactivity. Details of electrochemical studies on Pt_{Cl}/MC catalyst are still underway and will be reported elsewhere.

In conclusion, we have succeeded in direct observation of Pt particles inside the mesopores, and 1 nm or smaller sized Pt catalysts were well dispersed inside the pores of MC support. Further, the possibility to use mesopores as catalytic reaction space was indicated. We suppose that the size and stability of Pt inside the pore is key to improve and preserve much larger Pt surface area for oxygen reduction. Furthermore, we believe that MC support could be applied for the most promising alloy catalysts, and it might increase their activity and stability.

We thank "Fuel Cell Promotion Office of Agency of Natural Resources and Energy, Ministry of Economy, Trade and Industry (METI)" and "New Energy, Industrial Technology Development Organization (NEDO)" for support.

References and Notes

1 A. Thomas, F. Goettmann, M. Antonietti, *Chem. Mater.* **2008**, *20*, 738.
2 Y. H. Ng, S. Ikeda, T. Harada, T. Sakata, H. Mori, A. Takaoka, M. Matsumura, *Langmuir* **2008**, *24*, 6307.
3 E. P. Ambrosio, C. Francia, M. Manzoli, N. Penazzi, P. Spinelli, *Int. J. Hydrogen Energy* **2008**, *33*, 3142.
4 J. Ding, K. Y. Chan, J. Ren, F.-S. Xiao, *Electrochim. Acta* **2005**, *50*, 3131.
5 S. Tanaka, N. Nishiyama, Y. Egashira, K. Ueyama, *Chem. Commun.* **2005**, 2125.
6 C. Liang, Z. Li, S. Dai, *Angew. Chem., Int. Ed.* **2008**, *47*, 3696.
7 K. Kimijima, A. Hayashi, I. Yagi, *Chem. Commun.* **2008**, 5809.
8 A. Hayashi, H. Notsu, K. Kimijima, J. Miyamoto, I. Yagi, *Electrochim. Acta* **2008**, *53*, 6117.
9 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.
10 S. H. Joo, S. J. Choi, I. Oh, J. Kwak, Z. Liu, O. Terasaki, R. Ryoo, *Nature* **2001**, *412*, 169.
11 S.-H. Liu, R.-F. Lu, S.-J. Huang, A.-Y. Lo, S.-H. Chien, S.-B. Liu, *Chem. Commun.* **2006**, 3435.
12 K. Wikander, A. B. Hungria, P. A. Midgley, A. E. C. Palmqvist, K. Holmberg, J. M. Thomas, *J. Colloid Interface Sci.* **2007**, *305*, 204.
13 L. Calvillo, M. J. Lazaro, E. Garcia-Bordeje, R. Moliner, P. L. Cabot, I. Esparbe, E. Pastor, J. J. Quintana, *J. Power Sources* **2007**, *169*, 59.

Published on the web (Advance View) March 14, 2009; doi:10.1246/cl.2009.346